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Removal of Soluble Organic and Insoluble Organic and Inorganic Materials by Flocculation

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INTRODUCTION

Surface waters are generally contaminated with varying amounts of organic and inorganic matter. This matter can be either soluble or insoluble and in nature generally occurs in both forms simultaneously. Much of the organic and inorganic material is introduced by natural means; e.g., by some type of biochemical or erosive action of water on soils while other contamination is introduced to aqueous streams by various types of waste disposal of domestic or industrial origin. In either case the nature of the organic and inorganic contaminants is quite diverse and is dependent upon existing environmental conditions.

Most of the naturally occurring organic substances are large, complex molecules. Though poorly characterized they seem to contain a large amount of carboxylic compounds and other constituents such as humins, ulmins, polyphenols, etc. Many of these organic materials impart color to the waters which they contaminate and are not usually eliminated with any great facility through normal sedimentation or filtration practices. Two common color bodies which are found in surface waters are broadly classified under the heading of humic and fulvic acids. Packham[1] and Black[2, 3] have described in considerable detail these specific types of compounds. Under the humic acid class are included those materials which are precipitated from an alkaline extract of soil by mineral acids. When reconstituted, the humic acid solutions acquire a characteristic deep brown color. On the other hand, the fulvic acids remain in solution when an alkaline leach solution of a soil is acidified with mineral acids. In dilute solution, fulvic acids are distinguishable from the humic acids by their yellow color.

Another type of organic foulant which is found in many surface waters is lignin sulfonate. The principal source of this foulant is as a waste product from paper mills. During the chemical pulping operation the lignin of the wood is dissolved. When the wood liquor is eventually cooked in the acid sulfite process the lignin is converted to the salt of lignin sulfonic acid.

Other organic compounds introduced into surface waters are the products of waste disposal from domestic and industrial sources and account for considerable pollution in our streams today. One particular pollutant which has had widespread use in the home and in industry in the last decade is the synthetic detergent. Characteristic of this group of materials is branched alkyl benzene sulfonate (ABS). This material is presently being phased out by the large soap manufacturers and replaced by the more biodegradable linear alkyl benzent sulfonate.

While the removal of insoluble organic and inorganic materials from aqueous streams with polymeric flocculants is well known and is being practiced on an increasingly large scale in this country, the removal of soluble organic material via flocculation processes is less well known.[4, 5] An investigation which has been reported recently[6] involves the interaction of a cationic polyelectrolyte with soluble anionic charged organic foulants, particularly ABS.

In this study the removal with polyelectrolytes of both soluble organic and insoluble organic and inorganic materials is considered. Particular attentin is given to the use of Primafloc C-7, a polyamine bisulfate salt wtih a molecular weight of approximately $3 \times 10,^6$ which permits much greater removals to be attained than do other presently known cationic polyelectrolytes. Emphasis is placed upon the removal of soluble, anionic, organic foulants from aqueous streams. These materials are known to irreversibly foul conventional anion exchange resins. Economical removal of such anionic, organic foulants should increase considerably the useful life of such anion exchange resins.

Also in the field of waste treatment, recent activity has been devoted to the replacement of such inorganic materials as $FeCl_3$, $Fe_2(SO_4)_3$, $AlCl_3$, $Al_2(SO_4)_3$ and $Ca(OH)_2$ with cationic polyelectrolytes in conditioning various sludges prior to dewatering. There are several reasons for the desired replacement of such materials, some of which are: elimination of two chemical feeds, reduction in inventory of stored chemicals, less corrosive conditioning chemicals, elimination of a lime scaling problem on the filtration medium, improved filter yields

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FORMAL DISCUSSIONS

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Dr. Robert B. Dean—

The paper by Crook and Pollio presents data to support the use of Primafloc C-7. This is one substance from the group of water-soluble high polymers that are of great theoretical and practical interest in the flocculation of soluble organic and soluble and insoluble inorganic material. The paper is admittedly difficult to understand but that is less the fault of the authors than of the subject. What is more important, as Hans Zinsser pointed out, is not whether a thing is difficult to understand but whether, once understood, it makes any sense. The papers and discussion this morning are helping us to make sense out of flocculants.

First a word about nomenclature. I am very happy to see the use of the generic term "polymeric flocculants," which includes both the so-called "polyelectrolytes" and other high-molecular-weight, water-soluble polymers that are not ionized. As the speakers well know, the term "polyelectrolyte" includes another interesting group of substances, the ion-exchange resins. Some of these are built up from the same raw materials as the ionic flocculants. A better term than "polyelectrolyte" would be "ionic flocculant."

Regardless of name, the polymeric flocculants are a class of substances that, at high dilutions, cause solids suspended in water to flocculate together in reasonably rigid flocs. The important word is "rigid." If the flocs did not have rigidity, but allowed the particles to glide over one another to form a densely packed layer, you would not get filterability. The mechanism of flocculation appears to be that of attachment: one end of a flocculant molecule attaches to one particle and the other end to another particle. Let us look at the dimensions to see if this is realistic. Clay particles have a length of about 1 micron, or 10,000 Angstrom units, and are about 1 micron apart on the average. The mean length per carbon atom in a hydrocarbon chain is close to 1.4 Å, and the molecular weight of CH_2 in a chain is 14; so that for each unit of molecular weight, we conveniently have a length of about 0.1 Å. A molecular weight of 1 million gives us a carbon chain that, if fully extended, would reach across 100,000 Å, or 10 microns. Actually, chains are randomly twisted and mean molecular weights along the chain are greater than 14 because of side groups, but the order of magnitude is correct. For a single chain to bridge between particles in the micron range, the molecular weight must be close to 1 million. The paper bears this out. Polymer efficiency does increase with molecular weight, and Primafloc C-7 with a molecular weight of 3 million is highly efficient.

Since most natural colloids are negatively charged, simple theory tells us that flocculants should carry a positive charge or be cationic. Unfortunately for theory there are many highly successful flocculants that have no charge at all; e.g., ethylene oxide polymers with molecular weights also in the milions. Even worse for the theory is the existence of very satisfactory flocculants that have a negative charge. As we all know, adsorption does not depend only upon unlike charges, although they can help.

In our work, we recently studied the flocculation of powdered activated carbon dispersed in

wastewater from a secondary treatment plant. We used a broad spectrum of flocculants, and in one study, a high-molecular-weight, anionic, acrylic polymer was clearly superior. In a second study with a different water, Primafloc C-7 was superior. We suspect that because the effluent from a given plant will vary from day to day, the type of flocculant that will be most effective will also vary. There is no doubt that there is a high degree of specificity in the reaction between the flocculant and the fluid to be clarified. To date, unfortunately, theory does not help us to choose the most efficient type.

A further complication arises from the very shape of the response curves. The last slide Fig. 15) shows this in an extreme degree. Primafloc C-7 on the slurry gives a dramatic increase in filtration rate at 0.75 percent. Dropping the concentration to 0.65 percent, however, gives results that are hardly better than the "standard plant rate," and raising the concentration to 0.85 percent actually gives results that are worse than the standard. Since flocculation is an interaction between solid and flocculant, we would expect that any change in the concentration of the slurry would have to be matched by a corresponding change in the dose of flocculant. Obviously one could only use a flocculating system with such a sharp concentration maximum in a slurry that had very closely controlled properties. Fortunately maxima are rarely as sharp as in the last slide, but all too often twice the optimum dose has no beneficial effect at all. In the treatment of wastewaters whose composition may vary severalfold in the course of a day, a flocculating agent that has a broad maximum in the dose-response curve is essential.

The reaction of ABS with Primafloc C-7 parallels closely the reaction of ABS with methylene blue. In both cases a stoichiometric complex is formed between anions and cations. The methylene blue complex is soluble in water, but it is more soluble in chloroform, which extracts it from the water. The polycationic electrolyte forms a filterable floc with ABS only when both substances are present at high concentrations. At low concentrations, the complex is soluble and no doubt partially ionic. Whether the complex is present as single molecules or as colloidal aggregates is immaterial when one member is already of colloidal dimensions. When clay is added, the flocculating agent can stick to the solid at both ends and still complex with ABS in the middle. The clay ends then assist the formation of floc.

It is interesting to note that at low concentrations the soluble or dispersed ABS-cationic complex is stronger than the ABS-methylene blue complex. One consequence of this is that cationic high polymers interfere with the determination of ABS by the methylene blue test.

Other anionic water soluble organic substances such as humic acids also appear to be complexed by Primafloc C-7, according to the data presented. Again the presence of additional solids, such as clay or diatomaceous earth, to form a filterable floc seems to be necessary for good removals. Whether incomplete removals from dilute solution are due to the presence of a filterable colloidal complex or to the presence of non-complexing substances in the humic acid mixture is not obvious.

In closing, I would like to say a good word for the old-fashioned flocculants: alum, iron salts, and lime. Despite their sometimes higher cost, lower filtration rates, and voluminous sludge, these agents have the ability to remove phosphates from wastewater. Evidence continues to accumulate to show that phosphates are among the worst pollutants of surface water because of the way they stimulate obnoxious blooms of algae. Some algae can fix nitrogen, and all of them contribute to the BOD load when they die. If we are ever to have clean water, removal of phosphates from our streams is a problem that must be solved.

D. A. Dahlstrom—

I should just like to thank Messrs. Crook and Pollio for an excellent contribution to the technical literature on the mechanism and potential uses of synthetic flocculants. The paper gives a very good insight into the behavior of the polyelectrolyte flocculants as well as several interesting examples with constructive data on good possibilities for further usage of these chemicals to improve waste and water treatment.

Undoubtedly the applicability of synthetic polyelectrolytes will continue to increase not only in usage but in the additional problems they will be able to solve. Continual improvement in existing flocculants in their application is needed as well as even more powerful new synthetics to solve the many treatment problems that require solutions for successful or more economical results. Thus, I would certainly encourage additional work by the authors and others in this field.